

Synthesis and Fabrication of Graphene Quantum Dots-Polypyrrole (GQDs-PPy) Nanocomposites in Bioengineering Applications as Supercapacitors and Fluorescent Probes



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Abstract

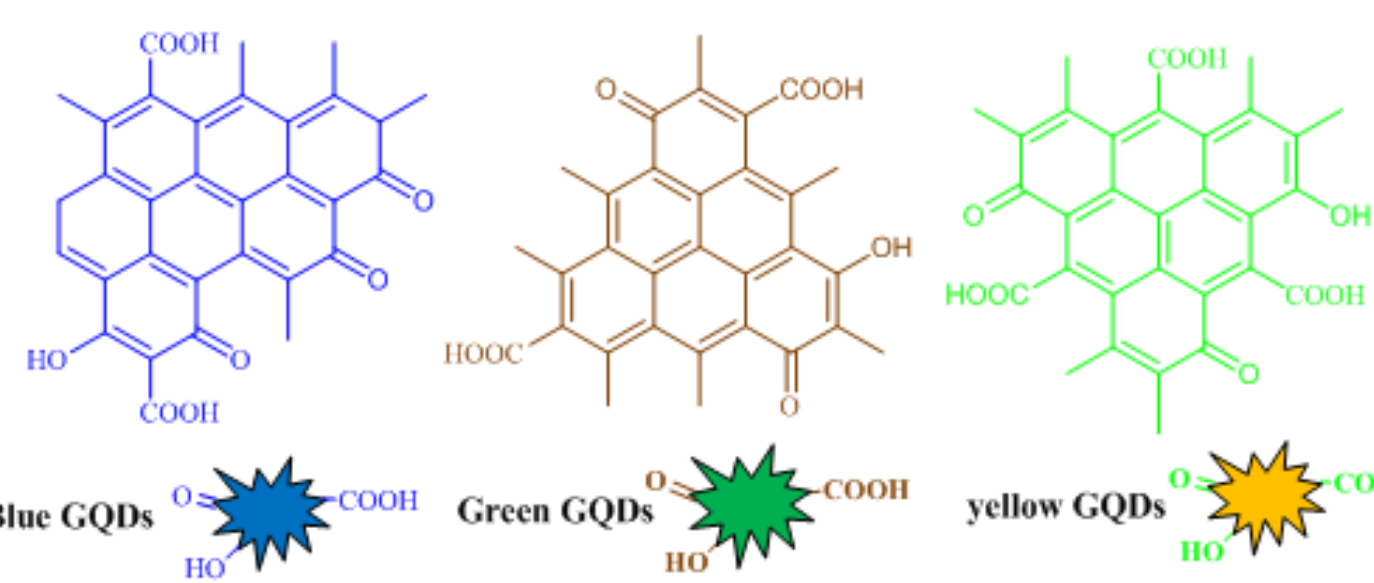
Graphene quantum dots (GQDs), which are edge-bound nanometer-size graphene pieces, have fascinating optical and electronic properties. These GQDs fabricated by acid treatment and chemical exfoliation of pitch carbon-fibres and this produced GQDs have 1-4 nm in size with 2D morphology. The photoluminescence of the GQDs can be tailored through varying the size of the GQDs by changing the process parameters. Due to the luminescence stability, nanosecond lifetime, biocompatibility, low toxicity, and high water solubility, these GQDs are demonstrated to be excellent probes for high contrast bioimaging and biosensing applications. Here, we reporting the fabrication of free standing GQDs-PPy hybrid electrode films by electrochemical polymerization for supercapacitor device assembly. And also we reporting the bioconjugated quantum dots (QDs) provide a new class of biological labels for evaluating biomolecular signatures (biomarkers) on intact cells and tissue specimens. In particular, the use of multicolor QD probes in immunohistochemistry or cell biology studies of proteins and peptides is considered to be the most important and clinically relevant applications.

1. Introduction

- Quantum dot nanoparticles generally fall within the 1-10 nm size range and possess size tunable, i.e. controllable, optical and electrical properties.
- Due their nano-size structures QDs exhibit substantial quantum confinement and edge effects.
- In comparison with organic dyes and fluorescent proteins, QDs have unique properties such as size-tunable light emission, superior signal brightness, resistance to photobleaching and simultaneous excitation of multiple fluorescence colors.
- These properties are most promising for improving the sensitivity and multiplexing capabilities of molecular histopathology and disease diagnosis.

2. Fabrication of GQDs

- GQDs are fabricated by acid treatment and chemical exfoliation of carbon fibres¹.



Scheme 1 Schematic representation of synthesis of GQDs by oxidation

Table 1: Different Types of GQDs based on their temperature

No.	Temperature	Size (nm)	Excited λ_{Max}	Emission λ_{Max}	Color emission
1	GQD-80 °C	8-10 nm	429 nm	564 nm	Yellow/orange
2	GQD-100 °C	4-7 nm	331 nm	500 nm	Green
3	GQD-120 °C	1-4 nm	318 nm	434 nm	Blue

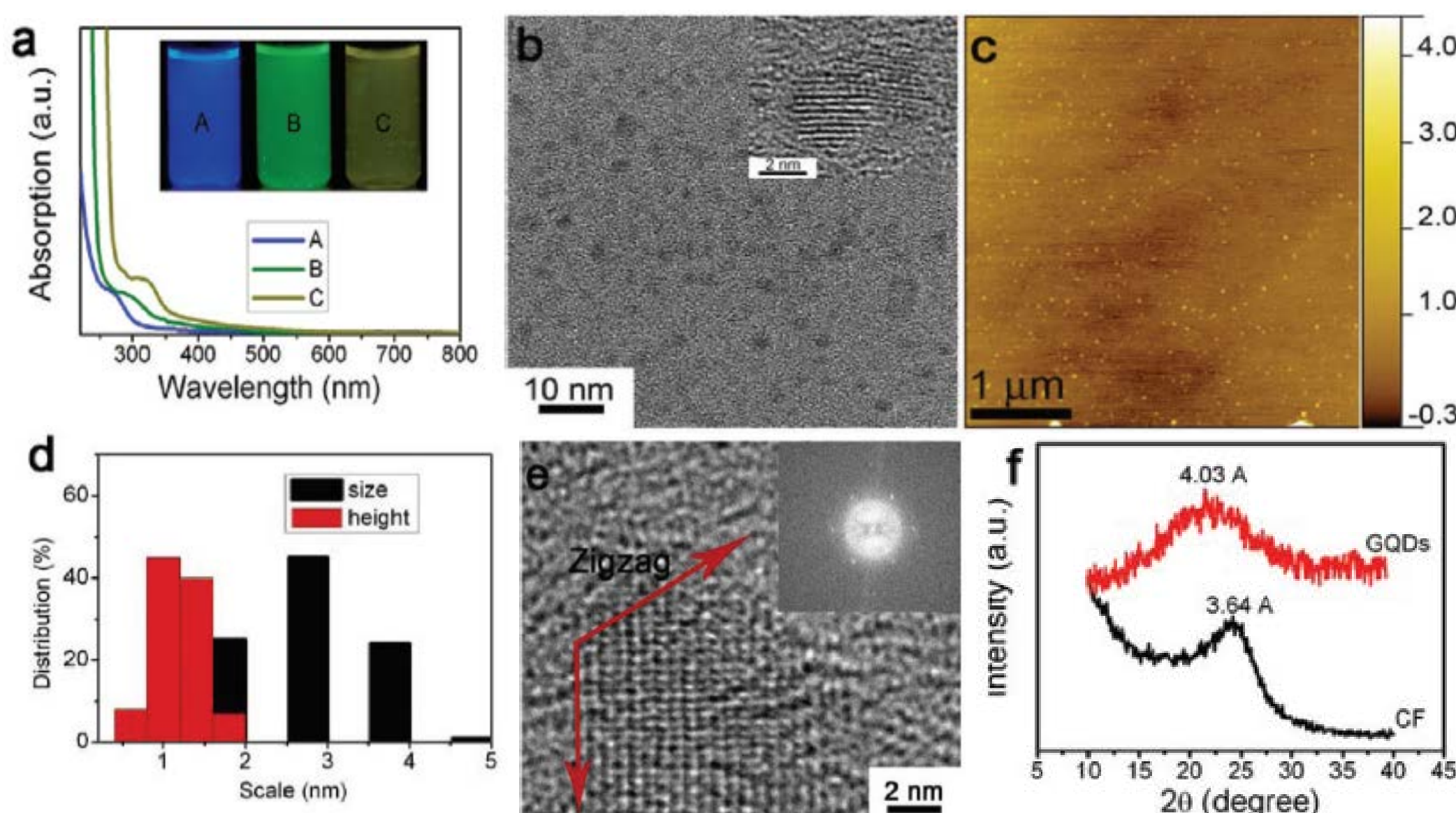


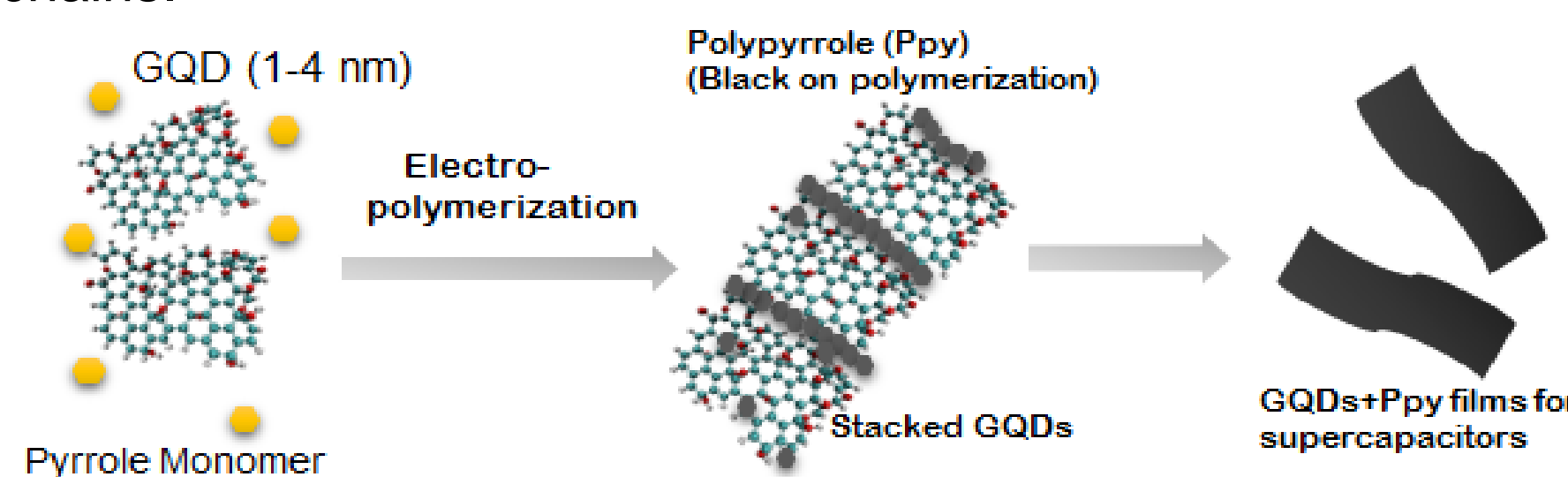
Fig 1: (a) UV-vis spectra of GQDs A, B, and C, corresponds to synthesized reaction temperature at 120, 100 and 80 °C respectively. (b) TEM images of GQDs (synthesized reaction temperature at 120 °C), inset of (b) is the HRTEM of GQDs. (c) AFM image of GQDs. (d) Size and height distribution of GQDs. (e) HRTEM image of the edge of GQD, inset is the 2D FFT of the edge.

6. References

1. Peng, J. *et.al*. Graphene quantum dots derived from carbon fibers. *Nano Letters* **12**, 844-849 (2012).
2. Aphale, A. *et.al*, 2015. Hybrid Electrodes by In-Situ Integration of Graphene and Carbon-Nanotubes in Polypyrrole for Supercapacitors. *Sci. Rep.* **5**, 14445 (2015).
3. Macwan, I., et al. Interactions between avidin and graphene for development of a biosensing platform. *Biosensors and Bioelectronics*, **89**, 326-333 (2017).

3. Fabrication of Supercapacitive Device

- Here, we report a facile *in-situ* fabrication of hybrid electrodes² via electrochemical polymerization (CV) of pyrrole containing GQDs.
- In this GQD-PPy nanocomposite, the electropolymerised polypyrrole (PPy) chains are uniformly distributed and intercalated with GQDs.
- It is observed that electrical conductivity can be increased by π - π stacking interaction among GQDs layers and aromatic rings of PPy chains.



Scheme 2: Schematic representation of GQDs-PPy electrodes fabrication process by cyclic voltammetry.

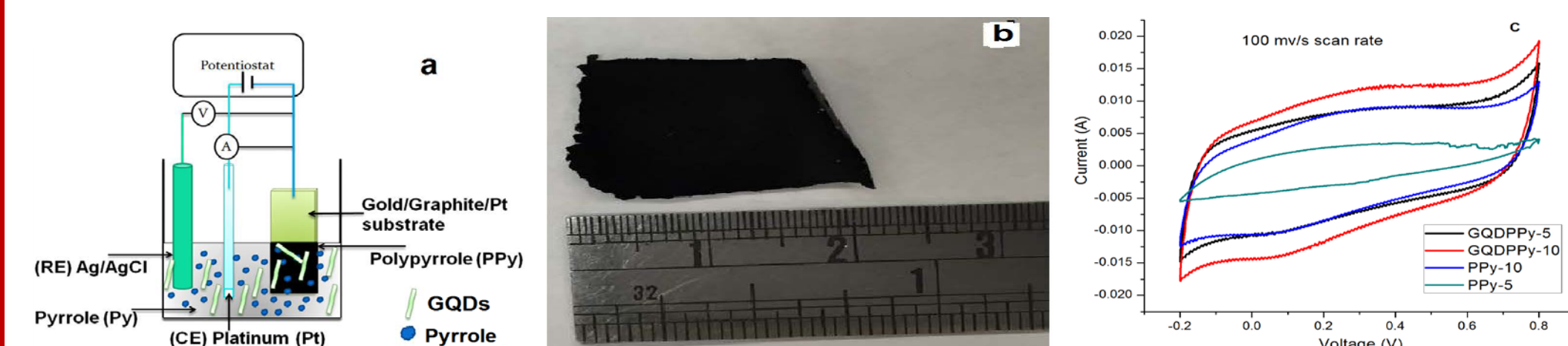
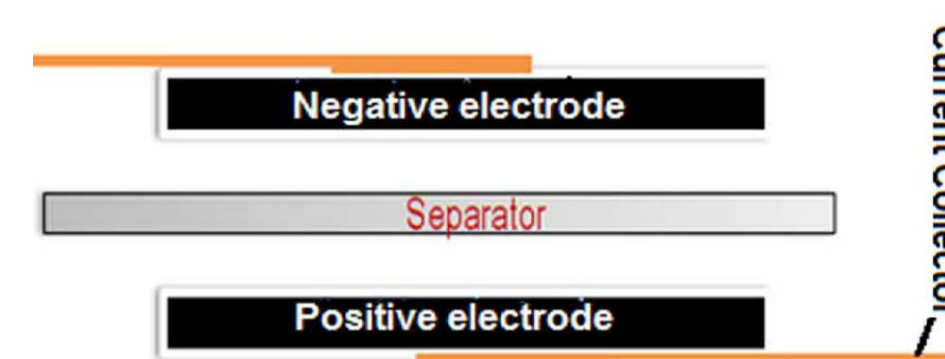


Fig 2: (a) Schematic representing of the CV and the fabrication process of the nanocomposite electrodes.

- CV parameters³:
 - ✓ Voltage : 800-900 mv
 - ✓ Scan rate: 10 and 100 mv/s
 - ✓ Cycles: 5, 10, 50, 100



4. Bioconjugated QDs as Fluorescent Probes

- QDs have broad excitation spectra, narrow emission spectra, long fluorescence time, negligible photo-bleaching, ability to conjugate with proteins and peptides by their functional groups, making them excellent probes for bioimaging applications.



Scheme 3: Synthesis of GQD-Succinidyl ester and GQD-Maleimide group

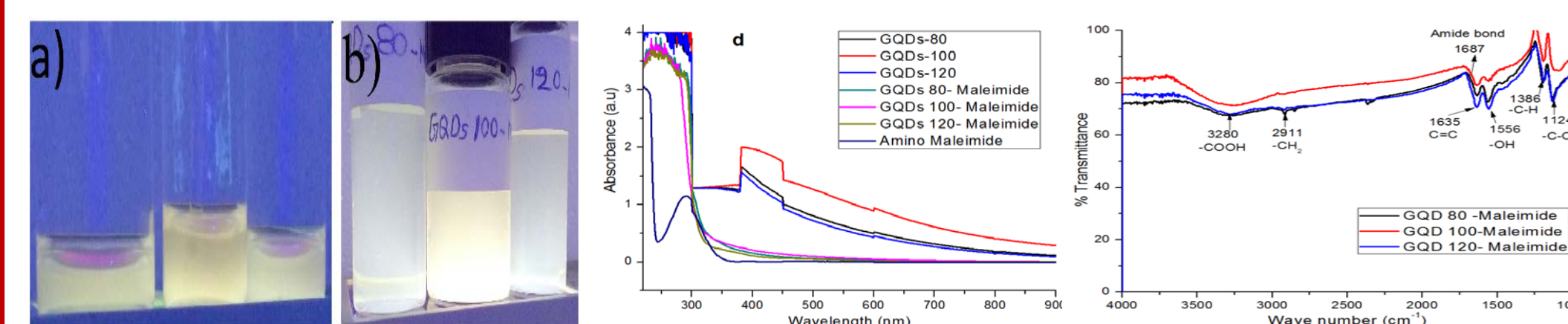


Fig 3: photographs of the water-dispersed GQDs illuminated under UV-Visible light at 365 nm. a) control GQDs and b) Functionalized GQDs-Maleimide, (c) UV-Visible spectra (d) FT-IR spectra of fluorescent probes.

5. Conclusion and Future Work

- The fabricated GQD-PPy hybrid electrodes showing high energy density and power density .
- This GQD-PPy electrode films can improve the performance of the supercapacitor device as well as its apparent use in biosensing for medical diagnostics.
- Due low cytotoxicity and excellent biocompatibility of these GQDs can be used as an eco-friendly material in biolabeling and bioimaging process.

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